

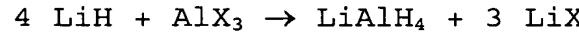


OZ 02054

Process for the preparation of lithium aluminium hydride solutions

The invention relates to a process for the preparation
5 of lithium aluminium hydride solutions.

Lithium aluminium hydride (LiAlH_4) is manufactured
industrially by reacting lithium hydride (LiH) with an
aluminium halide (AlX_3) by the Schlesinger method
10 (Finholt, A.F., Bond, A.C. and Schlesinger H.I.J., JACS,
69, 1199 (1947)):

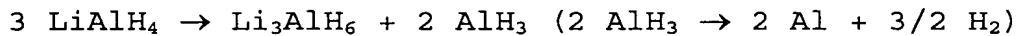


15 X is here F, Cl, Br or I, with Cl being the most usual.
Ethers are used as the solvent. Commercially available
 LiAlH_4 solutions generally contain no diethyl ether,
because of the associated risk of explosion, but are
manufactured as a 10% solution in THF or as a 15%
20 solution in THF/toluene.

In order to obtain a solution of LiAlH_4 in THF, the
synthesis may be carried out in THF. However, this has
the disadvantage, on the one hand that the aluminium
25 halides (preferably AlCl_3) utilised are poorly soluble in
THF, and on the other hand that the lithium halides
(preferably LiCl) which arise are relatively readily
soluble in THF. This process thus exhibits a relatively
low synthesis concentration and results in solutions
30 having a relatively high halide impurity content.

For this reason solutions of LiAlH_4 in THF are prepared
in such a way that the synthesis of LiAlH_4 is carried out
first in diethyl ether. This has the advantage that the
35 solubility of the aluminium halides (preferably AlCl_3) is
relatively high in diethyl ether, while conversely the
solubility of the lithium halides (preferably LiCl)
which arise is relatively poor in diethyl ether. The

LiAlH₄ solution in diethyl ether that is obtained is subsequently evaporated to dryness, and the solid LiAlH₄ powder is dissolved in the desired solvent (for example THF or THF/toluene). A disadvantage of this process is
5 that the thermal loading of the LiAlH₄ during evaporation results in a partial decomposition:



10 A further disadvantage of this process is apparent in that a solid is first prepared from a solution in energy-intensive manner, and is then dissolved again.

15 The object of the invention is to provide a process for the preparation of diethyl-ether-free LiAlH₄ solutions, which eliminates the disadvantages of the prior art and in particular avoids the isolation and re-dissolution of LiAlH₄.

20 The object is achieved by a process for the preparation of LiAlH₄ solutions, in which lithium hydride reacts with an aluminium halide in diethyl ether to give lithium aluminium hydride, the lithium halide which arises is separated, and wherein a solvent the complexing energy 25 of which with LiAlH₄ is greater than the complexing energy of diethyl ether with LiAlH₄ is then added, and the diethyl ether is removed by distillation.

30 Ethers such as, for example, tetrahydrofuran (THF), 2-methyltetrahydrofuran and ethers from the ethyl glycol ether group (such as, for example, monoglycol dimethyl ether, monoglycol diethyl ether, diglycol dimethyl ether, diglycol diethyl ether or diglycol dibutyl ether) may be utilised as preferred solvents. THF and 2-methyl-THF are particularly preferred. Amines, the complexing energy of which with LiAlH₄ is higher than the complexing energy of diethyl ether with LiAlH₄, may also be utilised. The complexing energies of intended

solvents will optionally need to be determined in preliminary tests.

- The process is preferably carried out in such a way that
5 when the reaction of LiH with AlX₃ (X = preferably Cl) in diethyl ether has taken place the synthesis solution, at preferably from 50 to 70°C, particularly preferably 55 to 65°C, so much diethyl ether is distilled off that preferably an approx. 20% solution of LiAlH₄ in diethyl
10 ether arises. The distillation of the diethyl ether is initially carried out at the boiling temperature of the diethyl ether. As the distillation proceeds further, the preferred temperatures are around 40 to 80°C, particularly preferably around 55 to 65°C. A vacuum is
15 preferably applied during the distillation. The preferred 20% concentration solution obtained corresponds to a complex of one mole LiAlH₄ with 2 mole diethyl ether. The solvent is then added. At least a quantity of solvent equivalent to the remaining diethyl
20 ether quantity (on a molar basis) is preferably added, particularly preferably from 2 to 5 molar equivalents. The diethyl ether released is distilled off. The distillation is preferably carried out with the application of a vacuum at preferred temperatures of
25 from 40 to 80°C, particularly preferably 55 to 65°C. In this manner the LiAlH₄ is subjected to only a comparatively low thermal load. In order to remove the diethyl ether completely, solvent may be after-charged and distilled off until such time as no further diethyl
30 ether is detectable in the LiAlH₄ solution. A larger quantity of solvent may also be added from the outset. The distillate obtained (diethyl ether and solvent) can be reutilised after rectification.
35 The 20% solution obtained is colourless and virtually clear. Decomposition products of LiAlH₄ are undetectable or barely detectable. When THF is used as the solvent, although the 20% solution is viscous, no LiAlH₄

crystallises out under refrigeration (down to - 20°C), so that such a solution may be marketed commercially. A 20% solution of LiAlH₄ may also be diluted with a hydrocarbon such as, for example, toluene (or xylene, mesitylene, cyclopentane, cyclohexane, methyl cyclohexane, pentane, hexane, heptane, octane). The hydrocarbon can also be added already to the reaction solution of LiAlH₄ in diethyl ether. The hydrocarbon is not disruptive to the subsequent addition of the solvent (which exhibits the higher complexing energy with LiAlH₄) and the distilling-off of the diethyl ether.

The advantage of the process according to the invention resides in that LiAlH₄ solutions (with a solvent other than diethyl ether) can be prepared directly from the synthesis solution by solvent exchange. The isolation of the LiAlH₄ by thermal drying, which is unfavourable in energy terms, and the associated losses by thermal decomposition are avoided in advantageous manner.

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The invention is explained hereinbelow in greater detail by reference to Examples.

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Example 1: Complexing of LiAlH₄ with THF, determination of complexing energies

4.0 g LiAlH₄ powder (103 mmol) in 222.5 g toluene at 20°C were placed in a 0.8-litre reactor under a nitrogen atmosphere. Using an RC1-model calorimeter from Mettler-Toledo, a temperature ramp from 20°C to 25°C was done and calibrated by means of electric calibration heating ($C_p = 1.94 \text{ kJ}/(\text{kg} \cdot \text{K})$), in order to determine the heat capacity of this mixture. 15.3 g diethyl ether (206 mmol) were then dispensed in at $T_{(i)} = 25^\circ\text{C}$ within 30 minutes, with 30 minutes' post-reaction. 14.9 g tetrahydrofuran (206 mmol) were then added to this solution within 30 minutes, with 30 minutes' post-reaction. A temperature ramp from 25°C to 20°C was done

and calibrated by means of electric calibration heating ($C_p = 1.97 \text{ kJ}/(\text{kg}^*\text{K})$), in order to determine the heat capacity of the total mixture of LiAlH₄, toluene, diethyl ether and THF. The mathematically determined complexing energies were as follows:

for step 1 (diethyl ether complexing):
 $\Delta H = -34.1 \text{ kJ/mol LiAlH}_4$

for step 2 (tetrahydrofuran complexing):
 $\Delta H = -35.0 \text{ kJ/mol LiAlH}_4.$

The LiAlH₄ already complexed by diethyl ether released further energy (35.0 kJ/mol LiAlH₄) when reacted with THF.

Example 2: Removal of diethyl ether by distillation from a solution of LiAlH₄ in diethyl ether and THF

250 g of the toluene-containing solution of LiAlH₄ with diethyl ether and tetrahydrofuran in a molar ratio of 1 : 2 : 2 (LiAlH₄ : diethyl ether : THF), which was prepared in 1, were distilled in an oil bath (80°C), initially at standard pressure (nitrogen atmosphere) and then under vacuum (up to 150 mbar). 169 g of a clear solution remained, which showed a molar ratio of diethyl ether : THF of 0.1 : 1. 1.7 g THF (2.3 mmol) were again added, and distillation took place again under the same conditions. Diethyl ether could no longer be detected by H-NMR spectroscopy in the solution obtained.

Example 3: Re-solvation of an LiAlH₄ / diethyl ether solution with THF

In a 500 ml reactor having a double-walled jacket 178 g THF (2475 mmol) were added at room temperature to 149 g of a 21% solution of LiAlH₄ in diethyl ether (825 mmol LiAlH₄ + 1650 mmol diethyl ether), corresponding to a

ratio of LiAlH₄ : diethyl ether : THF = 1 : 2 : 3. The solution was heated to boiling under a nitrogen atmosphere (internal temperature 60°C). When distillate had ceased to pass over at this temperature, a vacuum 5 was applied and the pressure was reduced gradually to 50 mbar. The distillation was finished when no further distillate passed over.

After breaking the vacuum with nitrogen, 143 g of a 10 clear solution containing 20.9 wt.% LiAlH₄ were obtained. Diethyl ether was no longer detectable in the H-NMR spectrum, the molar ratio of LiAlH₄ : tetrahydrofuran was 1 : 2.

15 **Example 4: Preparation of a 15% LiAlH₄ solution in THF/toluene**

48.2 g toluene were added to 123.1 g of the solution of LiAlH₄ in THF from Example 3 having an LiAlH₄ content of 20 677 mmol. The solution remained clear and colourless. The LiAlH₄ content was around 15 wt.%, the molar ratio of LiAlH₄ : tetrahydrofuran was 1 : 2.